

# **PREPARATION OF POLYAMIDE11/BAMBOO FLOUR POLYMER COMPOSITE USING POLYVINYL ALCOHOL AS COMPATIBILIZER**

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## **ABSTRACT**

In this work, the effects of bamboo flour (BF) and polyvinyl alcohol (PVA) contents on the tensile strength, impact strength, thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA) of polyamide 11/BF composites were studied in detail. The PVA was added into PA11/BF composites by two methods: (i) melt mixing with the other components in Haake mixer (one-step method); (ii) dispersing on the surface of BF in ethanol solution before mixing with PA11 in the melted state (two-step method). The investigation of mechanical properties showed the tensile strength of composites prepared by two-step method was higher than that of one-step method, while the trend for impact strength was opposite. On the other hand, DMTA analyses exhibited the enhancement of the compatibility of PA11/BF sample by observing the shift of peaks at the  $\beta$  relaxation around  $-80^{\circ}\text{C}$  due to the presence of PVA. This led to the increase of thermal stability of PA11/PVA/BF composites in comparison with PA11/BF composites.

**Keywords:** bamboo flour, PA11, poly vinylalcohol, DMTA, tensile strength.

## **1. INTRODUCTION**

Natural fibers are increasingly gaining in interest as reinforcing agents for composites, such as wood fibers, jute, hemp etc. These fibers own good mechanical properties and low density, therefore they are considered as a "green" solution in replacing traditional fibers such as glass fiber. Among them, bamboo fiber has many advantages such as high mechanical strength: tensile strength and modulus of elasticity can reach to 441.0 MPa and 35.9 GPa, respectively, while its density is quite low, about  $0.80\text{-}1.1\text{ g/cm}^3$  [1, 2]. Vietnam is a tropical monsoon country with many favorable conditions for growing up bamboo. Therefore, short bamboo fiber (bamboo flour-BF) can be supplied to industries with high quantity and low cost.

On the other hand, bio-polymers become more popular and are considered as potential substitution for conventional thermoplastics in manufacturing wood plastic composites (WPC). A major advantage of biopolymer is natural ingredients; therefore the usage of bio-polymers allows for preparing green composite materials such as WPC. However, like other

thermoplastics used for WPC fabrication, the drawback of bio-WPC is poor adhesion between bio-polymers and bamboo flour. BF is chemically treated or modified to improve its compatibility with the plastics. Sukmawan et al. used steam exploded bamboo (SEB) fibers which was treated with alkaline solution to improve compatibility with poly lactic acid (PLA) [3]. Lee et al. have improved the mechanical properties of PLA/bamboo fiber composite by using lysine-diisocyanate (LDI) as a coupling agent to modify the surface of BF [4]. As the isocyanate group content in LDI increased to 0.33 %, tensile strength and elastic modulus increased rapidly from 29.0 MPa to 42.0 MPa and from 2666 MPa to 2964 MPa, respectively.

One of the most common bio-plastics which used in the fabrication of WPC was polyamide 11(PA11). PA11 has high mechanical properties and a melting point of about 190 °C, therefore this could prevent thermal decomposition of WF during processing WPC. Several studies on the composite based on PA11 and cellulosic fibers have been carried out. In Patrick Zierdt's study, WF was treated with alkaline in order to increase hydroxyl group content of its [5]. The obtained results showed that PA11/wood flour significantly increased in the mechanical properties after the alkaline treatment. With 50 wt.% of WF, Young's modulus and tensile strength reached to 5049 MPa and 65 MPa, respectively, these values were higher than that of composite without treatment. In our previous study, the bamboo flour (BF) was modified with tetraethyl orthosilicate to improve the compatibility with PA11 matrix [6]. Therefore, modified BF enhanced the storage modulus and loss modulus of the PA11/BF composites in comparison with the original BF.

However, the main drawback in WF treatment was the solvents which discharged into the environment. Therefore, the use of compatibilizers in WPC material was considered as a green solution to reduce environmental pollution. In this work, polyvinyl alcohol (PVA) was used as a compatibilizer to improve the properties of PA11/BF composite. Tensile strength, impact strength, thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA) were performed in order to evaluate the effect of PVA on the matrix/filler compatibility.

## 2. EXPERIMENTALS

### 2.1. Materials and sample preparation

#### 2.1.1. Materials

Polyamide 11 (PA 11) was purchased from Akerma (Spain). PA11 has melting point of 186 °C and its density is 1.02 g/cm<sup>3</sup>. The BF (moisture lower than 8 %) of *Dendrocalamus barbatus* (North Vietnam) with diameter of 150 µm was provided by VNDD Ltd. (Vietnam). Polyvinyl alcohol was purchased from Sigma-Aldrich (America). Solution ethanol, 99.7 % and ammonia solution was purchase from Duc Giang chemical company (Vietnam).

#### 2.1.2. Sample preparation

**One-step method:** PA11, PVA were calculated and weighed (Table 1) in order to fill 75 % of mixing chamber volume. After that, this mixture was pre-mixed and dry in 80 °C for 12 hours. Next, the PA11/PVA/BF were prepared in chamber of Haake mixer at mixing temperature of 200 °C; mixing rotor speed of 50 rpm and mixing time of 5 minutes. Then, the above composites at melting state were pressed into thin sheets by using Toyo Seiky press machine (Japan). They were subjected for 2 minutes at a pressure of 5 MPa and at a

temperature of 200 °C. The final samples were cooled down and kept at room temperature at least one day before further characterization and analysis.

**Two-step method:** At first step, an amount of PVA was dissolved into 200 ml of distilled water by magnetic stirrer in 1 hour at 70 °C and stirring speed 500 rpm. After BF was dispersed completely in solution, keep stirring the solution for 45 minutes. The mixture was put into oven in order to remove the water to obtain the PVA modified BF to use in experiments. Second step, to prepare the samples as listed in Table 1, PA and PVA modified BF was calculated, weighed and mixed in the Haake mixer at mixing temperature of 200 °C; mixing rotor speed of 50 rpm and mixing time of 5 minutes.

Table 1. Components ratio and symbol of composite samples prepared by one-step method and two-step method.

No.	PA content (wt.%)	BF content (wt.%)	PVA content (wt.%)	sample symbols	
				one-step method	two-step method
1	70	30	-	PA30-0	PA30-0
2	60	40	-	PA40-0	PA40-0
3	50	50	-	PA50-0	PA50-0
4	65	30	5	PA30-5	PT30-5
5	55	40	5	PA40-5	PT40-5
6	45	50	5	PA50-5	PT50-5
7	60	30	10	PA30-10	PT30-10
8	50	40	10	PA40-10	PT40-10
9	40	50	10	PA50-10	PT50-10
10	55	30	15	PA30-15	PT30-15
11	45	40	15	PA40-15	PT40-15
12	35	50	15	PA50-15	PT50-15

## 2.2. Characterization

### 2.2.1. Tensile strength

The tensile test was conducted and obtained the average value by measuring each sample piece with five times at a crosshead speed of 50 mm/min in Zwick Tensiler 2.5 (Germany) according to ASTM D 638 standard.

### 2.2.2. Izod impact strength

The Izod impact test was conducted and obtained the average value by measuring each sample piece with three times by Testresources equipment (America) according to standard ASTM D 256.

### 2.2.3. Thermal gravimetric analysis (TGA)

The thermal gravimetric analysis (TGA) were conducted on TGA 209F1 (Shimadzu, Japan) with heating rate of 10 °C/min under nitrogen flow, from room temperature up to 600 °C.

### 2.2.4. Dynamic mechanical thermal analyse (DMTA)

The thermal behaviour of the composites were determined by dynamic mechanical thermal analyses (DMTA) using DMTA MCR 302. Rectangular samples of dimension  $50 \times 10 \times 0.65$  mm were used for the test. The measurements were done from  $-100^{\circ}\text{C}$  to  $120^{\circ}\text{C}$ , with a heating rate of  $3^{\circ}\text{C}/\text{min}$ , under nitrogen flow, at a frequency of 1 rad/s and a dynamic strain of 0.1 %.

### 3. RESULTS AND DISCUSSION

#### 3.1. Tensile strength (Rb)

Tensile strength of PA11 was 37.5 MPa that slightly decreases after mixing with BF.

Table 2. Tensile strength (MPa) of PA11/PVA/BF composites.

BF contents (%.w)	PVA contents(%.w)						
	0	5		10		15	
	one-step method	one-step method	two-step method	one-step method	two-step method	one-step method	two-step method
30	35.6	35.8	36.1	36.3	37.7	34.7	34.9
40	39.1	39.6	40.5	40.6	41.5	39.9	40.8
50	36.5	37.4	37.6	38.2	39.6	37.3	37.5

When the content of BF in composites were 30 wt.% and 40 wt.%, the tensile strength reached to 35.6 MPa and 39.1 MPa, respectively. However, the tensile strength of composite decreased when using 50 wt.% of BF. BF at 40wt.% gave the optimum dispersibility in composite that agreed with other research [7]. By using the compatibilizer PVA, tensile strength of composite samples increased as listed in Table 2. The increase might be due to the hydrogen interaction of hydroxyl groups in PVA and cellulose, therefore the dispersibility of WF in matrix become finer.

The tensile strength of composites prepared by one-step method recorded lower values than that of composites prepared by two-step method. Especially, PT40-10 sample owned the highest tensile strength (41.5 MPa) in comparison with PA40-10 (40.6 MPa). This increase can be explained that the modification in solution of two-step method improved the dispersibility and adhesion of PVA on surface of BF. When PVA content was higher than 10 wt.%, the excess amount of PVA caused the phases isolation and reduced the adhesion of PVA and BF. This led to the dramatically decrease of tensile strength of samples that prepared by both methods.

#### 3.2. Impact strength of composites

Effect of BF and compatibilizer PVA on impact strength of PA/PVA/BF were shown in Fig. 1. At the same PVA contents of 10 wt.%, the impact strength of composites decreased when increased BF contents. For example, the tensile strength of PA30-10 sample was 22.52 J/m in comparison to 11.05 J/m of PA50-10 sample. This can be explained that the presence of BF increased the rigidity of composites, thus the samples would be broke down under high impact load. The impact strength of composites were enhanced by adding PVA. For instances, the

impact strength of PVA40-10 (15.70 J/m) is higher than that of PVA40-0 (20.72 J/m) and PT40-10 (19.43 J/m). The results showed that the optimum tensile strength and impact strength can be achieved by using contents of PVA 10 wt.% BF 40 wt.%.

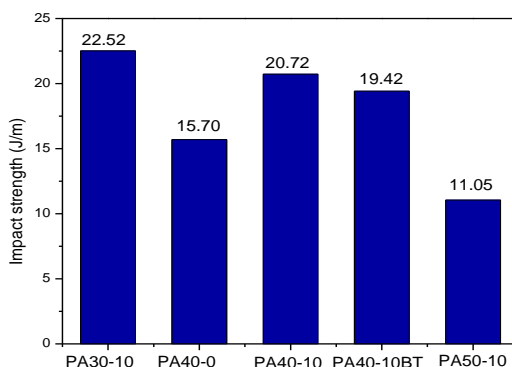


Figure 1. Impact strength of composite samples at various BF contents.

### 3.3. Thermal gravimetric analysis of composites

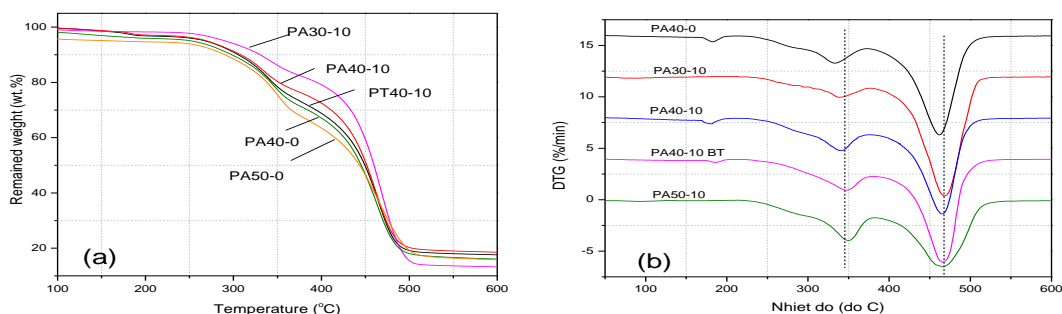


Figure 2. (a) TG and (b) DTG diagrams of PA/bamboo flour composites with different content of PVA and bamboo flour.

To evaluate the effect of PVA as a compatibilizer and bamboo flour content on the thermal stability of PA/bamboo flour composites, these composites were analysed by TGA method from room temperature to 600 °C in nitrogen gas environment. The TG and DTG diagrams and thermal parameters obtained from TGA data were presented in Fig. 2 (a), (b) and Table 3.

Observably, the PA/bamboo flour composites were degraded according to three stages corresponding to three steps of weight loss as shown in TG diagrams. The first stage of degradation process in the range from room temperature to around 250 °C can be attributed to the evaporation of free water in the composites (about 3 wt.%). Then, the decomposition process of PA chains, lignin and a part of hemicellulose and cellulose occurred from 250 °C to 370 °C, corresponding to a weight loss of ca. 23 wt.% [8]. Finally, the complete degradation of PA chains and cellulose was recognized at the last stage with a weight loss of ca. 56 wt.%.

As seen in Fig. 2 (a), the bamboo flour content caused a strong effect on the thermal stability of the PA/bamboo flour composites. For example, the weight loss of PA30-10, PA40-10 and PA50-10 at the same PVA concentration in first stage degradation was 3 wt.%, 4 wt.% and 6 wt.%, respectively, while in the second stage, the weight loss of these composites were 18 wt.%, 27 wt.% and 32 wt.%.

In comparison with PA/bamboo flour composite containing 40 wt.% of PA content and 10 wt.% of bamboo flour with and without PVA, the onset degradation temperature of the composite in the presence of PVA (PT40-10, 303.5 °C) is higher than that of the composite without PVA (PA40-10, 309.5 °C). This means that PVA could improve the compatibility of PA and BF, as a result, the thermal stability of the composite containing PVA becomes better. The degradation temperature of the composites shifted to higher temperature as increasing the BF content. However, because of the difference in hydrophobicity of BF and PVA, the remained weight at 550°C of the composite containing PVA and BF was lower than that of PA40-0 (Table 3).

The maximum degradation temperature of the composites obtained from DTA diagrams (Fig. 2(b)) and listed in Table 3. The PA40-0 had two maximum degradation temperature values ( $T_{max1}$  and  $T_{max2}$ ) at 332 °C and 462 °C. As using PVA as a compatibilizer, the maximum degradation temperature of the composites had a slightly increase tendency. For instance, the maximum degradation temperature of the PA40-10 was 339.5 °C and 464.8 °C while that of PT40-10 was 347.4 °C and 465.4 °C. This result confirmed the role of PVA in enhancement the thermal stability of the composites.

Table 3. Thermal parameters of the PA/bamboo flour composites.

Sample	$T_{oc}$ (°C)	$T_{max1}$ (°C)	$T_{max2}$ (°C)	Remained weight at 550 °C (wt.%)
PA40-0	303.5	332.5	462.0	17.3
PA30-10	303.1	347.3	467.9	16.5
PA40-10	304.8	339.5	464.8	15.7
PT40-10	309.5	347.4	465.4	15.8
PA50-10	316.0	349.7	466.0	15.2

### 3.4. Dynamic mechanical thermal analysis

Figure 3 showed the dependence of the modulus storage  $G'$  and loss modulus  $G''$  of PA40-0, PT40-10 and PA40-10 composites on temperature between -100 °C and 120 °C. For PA40-0, there are two peaks that observed in the Fig. 3 (a) [9]. The first peak at -80 °C associated with  $\beta$  relaxation of the free amide groups in the PA11. And the second peak at about 30 °C involved glass transition temperature of PA11 ( $\alpha$  relaxation) [10]. From the Fig. 3 (a), a slight increase in the storage modulus was observed due to introduce of PVA. This might due to the increase in the stiffness of matrix with the positive effect imparted by the PVA that allowed the fine dispersion of BF and a greater degree of stress transfer at the interface. It could be explained why the glassy modulus of PT40-10 sample was always higher than that of PA40-10. In addition, the modulus of PA40-10 and PT40-10 samples in the rubbery phase were recorded higher than that of PA40-0, indicating that PVA had an influence on either the glassy or rubbery phase of the composites. This result reflects the role of PVA which has improved the dispersion of BF in the PA resin, especially for composite using two-step method.

Figure 3 (b) showed the relation between the loss modulus and the temperature of the samples PA40-0, PA40-10 and PT40-1. The  $\beta$  relaxation of PA40-0 composite was initially observed at -80 °C. By adding PVA, the oscillation clearly shifted from -90 °C to -81 °C for both PA40-10 and PT40-10 samples. Besides, the magnitude of peak increased with the presence

of PVA that caused by the slight increase of water uptake leading to an interaction between water and the polar groups of PA11 [10].

For  $\alpha$  relaxation, the maximum of the peak was recorded at 30 °C for PA40-0 sample. This data was consistent with Tg of pure PA11 [6]. However, the expansion of peak around 30 °C reflected the existence of two regions (neat PA11 and BF) in the amorphous phase. Contrarily, a relatively sharp peak of  $\alpha$  relaxation at higher temperature was observed for PA40-10 and PT40-10 samples. The shift of the relaxation indicated a higher homogeneity of rubbery state due to introduction of PVA.

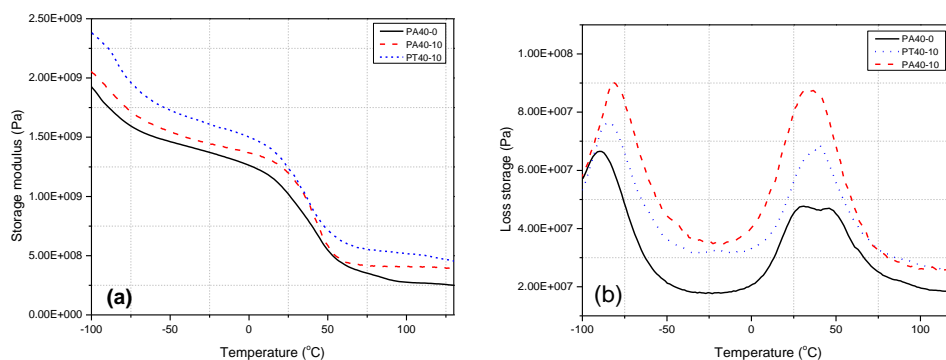


Figure 3. (a) Storage modulus  $G'$  and (b) loss modulus  $G''$  of PA40-0, PA40-10 and PT40-10 samples.

#### 4. CONCLUSION

The results in this research showed that PVA compatibilizer has improved mechanical properties. PT40-10 sample reached to the highest tensile strength and impact strength at 41.5 MPa and 19.42 J/m, respectively. Likewise, the figures for PA40-10 samples were 40.6 MPa and 20.72 J/m. The TGA data highlight that there was a slightly improvement on thermal stability of composites by using PVA. Besides, DMTA analysis showed that PVA increased in the storage modulus  $G'$  of composite. The shift of temperature of  $\beta$  and  $\alpha$  relaxation reflected a higher homogeneity of PT40-10 and PA40-10 composites in comparison with PA40-10.

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